ELECTROPHORESIS OF POLYELECTROLYTES WITH PARTIAL DRAINAGE.

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The electrophoretic velocity of a uniformly charged porous sphere in a salt solution is considered to be composed of three contributions. These are.
1. a motion caused by that part of the charge which is exactly compensated by counter-ions within the porous sphere.
2. a motion caused by the net charge of the porous sphere.
3. a motion caused by the counter-ions outside the sphere.

The influence of relaxation is left out of consideration. The presence of the counter-ions is shown to lead to a relatively high degree of draining. In solutions of high ionic strength, where the porous sphere model fails, poly-electrolyte coils are shown to be freely drained and the application of Henry's theory of electrophoresis of a cylindrical rod is discussed.

§ 1.   Introduction.

In recent years the properties of polyelectrolytes, such as polyacrylic acid, gum arabic and many others, have been the subject of experimental and theoretical study. It is of considerable interest to investigate the electrophoretic behaviour of these compounds.

The theoretical treatment in this paper is based on the porous sphere model introduced by *Debye* and *Bueche* [1]) and by *Brinkman* [2]) in their theory of sedimentation and viscosity of partially drained polymer coils **).

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[1]) *P. Debye* and *A M Bueche*, J. Chem. Phys. **16**, 573 (1948).
[2]) *H. C. Brinkman*, Proc. Koninkl. Ned. Akad. Wetenschap. **50**, 618, 821 (1947).
[3]) *J. J. Hermans* and *H. Fujita*, Proc. Koninkl. Ned. Akad. Wetenschap. **B 58**, 182 (1955).
[4]) *J. J. Hermans*, private communication.

The polymer chain with Z elementary charges is replaced by N beads. Each bead has a friction factor f and an electric charge Ze/N. The beads are distributed evenly over a sphere with radius R. The density of the beads is hence $\nu = N/^4/_3\pi R^3$ inside the sphere and $\nu = 0$ outside the sphere. The countercharge is found inside and outside the sphere. Its distribution, assumed to be continuous, depends on $\varkappa R$, $\varkappa$ being the reciprocal thickness of the ionic atmosphere as defined in the theory of *Debye* and *Hückel*.

When the sphere is subjected to electrophoresis in an extraneous electric field $\vec{E}$, the velocity $\vec{v}$ of the liquid with respect to the beads must obey the equations

$$\eta \Delta \vec{v} - \text{grad } p - \nu f \vec{v} + \varrho \vec{E} = 0 \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{div } \vec{v} = 0$$

η is the viscosity of the liquid. p the hydrostatic pressure and ϱ the density of the countercharge.

The term $-\nu f \vec{v}$ in (1) represents the force exerted by the beads on the liquid and vanishes outside the sphere.

Assuming that the electric conductivity is the same inside and outside the sphere, the applied field $\vec{E}$ is not perturbed by the sphere. Then the condition for steady motion is

$$Z e \vec{E} + \int \vec{v} \nu f d\tau = 0 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In order to solve eq. (1) for $\vec{v}$, with condition (2), the density ϱ of the countercharge must be known. We shall neglect the change of ϱ due to the relaxation effect and furthermore assume that the Debye-Hückel approximation is valid. This enables us to use the results of *Hermans* and *Overbeek* [5]. Their expression for the potential outside the sphere can be cast in the form

$$\psi_r = \frac{Z_{eff} e}{\varepsilon r} \frac{e^{-\varkappa(r-R)}}{1 + \varkappa R} \quad r > R \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{with } Z_{eff} = Z \frac{3}{2 \varkappa^3 R^3} \Big\{ (1 + \varkappa R)^2 e^{-2\varkappa R} - 1 + \varkappa^2 R^2 \Big\} . \quad . \quad (4)$$

r is the distance from the centre of the sphere.

Eq. (3) represents the potential field around a solid sphere with charge $Z_{eff} e$. Obviously the effective charge $Z_{eff} e$ of the porous sphere consists of the fixed charge Ze and a countercharge $-(Z - Z_{eff}) e$.

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[5] *J. J. Hermans* and *J. Th. G. Overbeek*, Rec. trav. chim. **67**, 761 (1948).

For the following calculations this countercharge inside the sphere is assumed to be smeared out uniformly. For the local density of the countercharge inside the sphere we hence employ the average value

$$\overline{\varrho} = - \frac{(Z - Z_{eff})e}{{}^{4}/_{3} \pi R^{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This approximation will be discussed later.

In the mathematical analysis the velocity of the sphere is put equal to zero. The velocity of the liquid at infinite distance, $-\overrightarrow{u}$, then gives the desired electrophoretic velocity $\overrightarrow{u}$.

In order to solve eq. (1) the volume force

$$-\nu f\overrightarrow{v} + \varrho\overrightarrow{E}$$

is split up into three components. Each component gives a contribution to $\overrightarrow{u}$, which can be written down immediately by using solutions of related problems, in particular the sedimentation of the porous sphere and the electrophoresis of the solid sphere.

The treatment of this model is straightforward. However, the connection between the model and an actual polyelectrolyte coil is to some extent arbitrary and introduces certain errors. One source of error is the neglect of the microscopic inhomogeneities in the distribution of the countercharge in a polyelectrolyte coil. Actually each charged monomer is surrounded by its atmosphere of ions; these give rise to a local Debye-Hückel-Onsager type of interaction, which increases with the ionic strength. This interaction is not accounted for in the present theory because both the countercharge and the beads are considered to be smeared out. The range of validity of the model results will be discussed and a different approach will be suggested for the case of high ionic strength.

§ 2. The electrophoresis of the porous sphere.

In the evaluation of the liquid velocity the electric charges are divided into the following parts:

1. The countercharge inside the sphere with a constant density $\overline{\varrho}$, given by eq. (5), together with an equivalent part of the fixed charge, with density $-\overline{\varrho}$.
2. The remainder, $Z_{eff}e$, of the fixed charge.
3. The countercharge outside the sphere, total $-Z_{eff}e$.

Each of these charge distributions is considered separately and their

contributions to the liquid velocity at infinite distance, $-\vec{u}_1$, $-\vec{u}_2$ and $-\vec{u}_3$ respectively, are evaluated, the sphere being at rest in all cases. The electrophoretic velocity of the sphere is then found as

$$\vec{u} = \vec{u}_1 + \vec{u}_2 + \vec{u}_3.$$

1. The liquid velocity $\vec{v}_1$ due to the first part of the charge should satisfy the equations

$$\eta \varDelta \vec{v}_1 - \mathrm{grad\ } p_1 - \nu f \vec{v}_1 + \varrho \vec{E} = 0 \ . \ . \ . \ . \ . \quad (6)$$
$$\mathrm{div\ } \vec{v}_1 = 0$$

The driving force on the fixed charges, with density $-\varrho$, is equal to

$$-\frac{4\pi}{3} R^3 \varrho \vec{E} = (Z - Z_{\mathrm{eff}}) e \vec{E}.$$

In view of eq. (2) we therefore also impose the condition

$$(Z - Z_{\mathrm{eff}}) e \vec{E} + \int \vec{v}_1 \nu f d\tau = 0 \ . \ . \ . \ . \ . \quad (7)$$

Inside the sphere the fixed and the mobile charges exert equal but opposite forces on the liquid; outside the sphere no force is exerted. Consequently the velocity and the pressure are constant, the first two terms of eq. (6) are zero and the velocity is derived from the remainder of eq. (6).

$$-\nu f \vec{v}_1 + \varrho \vec{E} = 0 \ . \ . \ . \ . \ . \ . \quad (8)$$

With the aid of the definition for ν and eq. (5) for $\bar{\varrho}$ eq. (8) is transformed into

$$\vec{v}_1 = -\frac{(Z - Z_{\mathrm{eff}}) e \vec{E}}{Nf} \ . \ . \ . \ . \ . \ . \ . \quad (9)$$

The first part of the electrophoretic velocity is therefore

$$\vec{u}_1 = \frac{(Z - Z_{\mathrm{eff}}) e \vec{E}}{Nf} \ . \ . \ . \ . \ . \ . \ . \quad (10)$$

or, in words, the velocity is the ratio of the total force on the fixed charge to the sum of the individual resistances of the beads. There is no interaction between the beads. With respect to this part of the motion the sphere behaves as if freely drained.

2. The second part involves the driving force $Z_{eff}e\vec{E}$ only.

The liquid velocity $\vec{v}_2$ should obey the equations

$$\eta\Delta\vec{v}_2 - \text{grad } p_2 - \nu f\vec{v}_2 = 0 \quad . \quad . \quad . \quad . \quad (11)$$

$$\text{div } \vec{v}_2 = 0$$

with the condition

$$Z_{eff}e\vec{E} + \int \vec{v}_2 \nu f d\tau = 0 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The driving force is distributed uniformly over the beads as. for instance, in the case of sedimentation. This case is identical with that of the porous sphere subject to a sedimentation force $Z_{eff}e\vec{E}$. Consequently the second contribution to the electrophoretic velocity is

$$\vec{u}_2 = \frac{Z_{eff}e\vec{E}}{F} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where F denotes the friction factor of the porous sphere in sedimentation.

For the case of sedimentation eq. (11) and (12) have been solved by *Debye* and *Bueche* [1]) and by *Brinkman* [2]). Their expression for F may be written as

$$\frac{F}{Nf} = \frac{9}{2\sigma^2} \frac{1 - \frac{1}{\sigma}\tanh \sigma}{1 + \frac{3}{2\sigma^2}(1 - \frac{1}{\sigma}\tanh\sigma)} \quad . \quad . \quad . \quad . \quad (14)$$

with

$$\sigma^2 = \frac{3Nf}{4\pi\eta R} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

3. The last component of the liquid velocity, $\vec{v}_3$, concerns the countercharge outside the sphere, with no force exerted inside the sphere. The differential equations inside the sphere

$$\eta\Delta\vec{v}_3 - \text{grad } p_3 - \nu f\vec{v}_3 = 0 \quad . \quad . \quad . \quad . \quad (16)$$

$$\text{div } \vec{v}_3 = 0$$

are satisfied by putting $\vec{v}_3 = 0$ in this region.

Outside the sphere the differential equations are

$$\eta\Delta\vec{v}_3 - \text{grad } p_3 = \varrho\vec{E} = 0 \quad . \quad . \quad . \quad . \quad (17)$$

$$\text{div } \vec{v}_3 = 0$$

Hückel[6]) and *Onsager*[7]) have solved eq. (17) for the electrophoresis of a solid sphere. As argued above ϱ in eq. (17) is identical with the density of the countercharge around a solid sphere with charge $Z_{eff}e$. $\vec{u_3}$ is thus equal to the electrophoretic effect on a $(Z_{eff}e)$ valent ion with radius R, which is given by

$$\vec{u_3} = -\ \frac{Z_{eff}e\vec{E}}{6\pi\eta R}\ \frac{\varkappa R}{1+\varkappa R} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Finally the electrophoretic velocity of the porous sphere is obtained by adding the velocity terms of eq. (10), (13) and (18)

$$\vec{u} = \left\{\frac{Z-Z_{eff}}{Nf} + \frac{Z_{eff}}{F} - \frac{Z_{eff}}{6\pi\eta R}\ \frac{\varkappa R}{1+\varkappa R}\right\}e\vec{E} \quad . \quad . \quad . \quad (19)$$

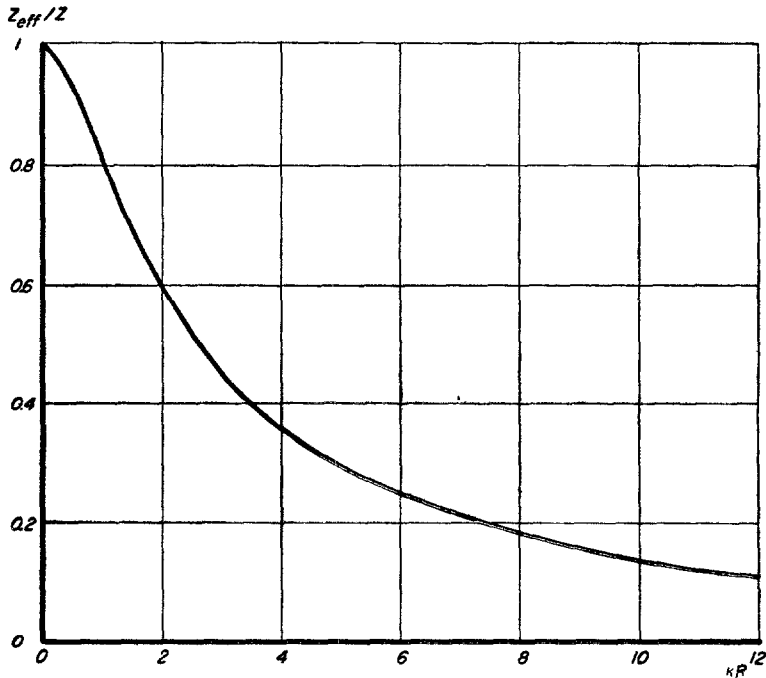It has been shown already that the factors Z_{eff} and F can be expressed in terms of the fundamental parameters Z, R, $\varkappa$ and Nf.

Fig. 1. Total charge inside the sphere as a function of $\varkappa$R.

[6]) *E. Hückel,* Physik. Z. **25,** 204 (1924).

[7]) *L. Onsager,* Physik. Z. **27,** 388 (1926); **28,** 276 (1927).

The effective charge is given in eq. (4). Fig. 1 presents Z_{eff}/Z as a function of $\varkappa R$. For $\varkappa R = 0$ there is no countercharge inside the sphere and $Z_{eff} = Z$. For $\varkappa R = \infty$ the total fixed charge is neutralised by the countercharge inside the sphere and $Z_{eff} = 0$.
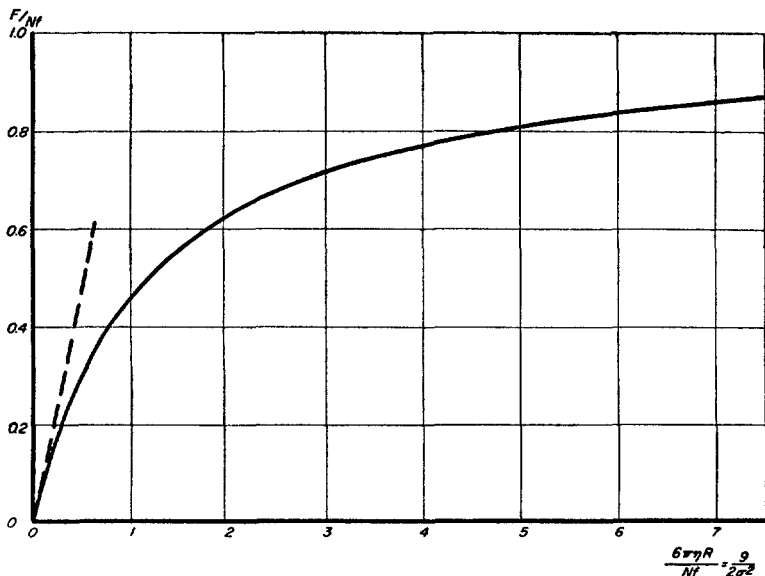

Fig. 2. Friction factor of porous sphere as a function of degree of drainage. Broken line: solid sphere.

The friction factor of the porous sphere in sedimentation is expressed in eq. (14). In fig. 2 F/Nf is plotted against

$$\frac{9}{2\sigma^2} = \frac{6\pi\eta R}{Nf}$$

For very large values of $\dfrac{6\pi\eta R}{Nf}$

the friction factor F approaches the free drainage value Nf. When

$$\frac{6\pi\eta R}{Nf} \to 0$$

the porous sphere behaves like a solid one and F attains the Stokes value $6\pi\eta R$.

Using the expressions for Z_{eff} and F, fig. 3 has been constructed, in which the electrophoretic mobility is shown as a function of $\varkappa R$ for various values of $6\pi\eta R/Nf$. The limiting values are easily recognized with the help of the special cases of Z_{eff} and F discussed above.
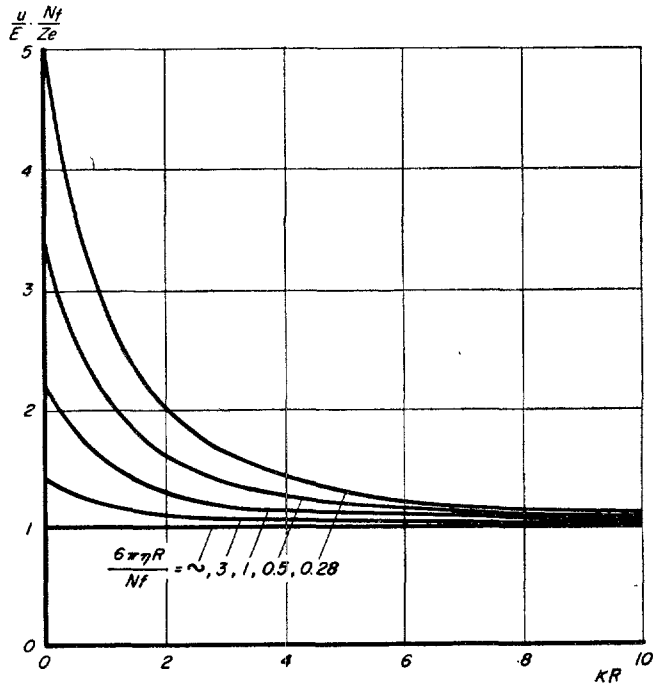
Fig. 3.   Electrophoretic velocity of the porous sphere
for various degrees of drainage.

a. For $\varkappa R = 0$ the countercharge is at infinite distance from the
sphere and has no influence on its motion. The velocity of the sphere
with friction factor F subject to the driving force $Ze\vec{E}$ is in this case

$$\vec{u} = \frac{Ze\vec{E}}{F}$$

b. For $\varkappa R = \infty$ the treatment for $\vec{u}_1$ can be followed with $Z_{eff} = 0$.
The obvious result is

$$\vec{u} = \frac{Ze\vec{E}}{Nf} \,.$$

The porous sphere behaves as if it were freely drained.
   c. In sedimentation the sphere is freely drained when

$$\frac{6\pi\eta R}{Nf} \to \infty \,.$$

In this case $F = Nf$ and eq. (19) for any value of $\varkappa R$, gives

$$\vec{u} = \frac{Ze\vec{E}}{Nf}$$

This shows that when there is no interaction between the beads in sedimentation, there is no interaction in electrophoresis either.

d. The porous sphere becomes impermeable if

$$\frac{6\pi\eta R}{Nf} \rightarrow 0$$

Then $F = 6\pi\eta R$, the term $Z - Z_{eff}/Nf$ may be neglected with respect to the other terms and eq. (19) converts correctly into the Hückel expression for the electrophoresis of a solid sphere [6])

$$\vec{u} = \frac{Z_{eff}e\vec{E}}{6\pi\eta R(1+\varkappa R)} = \frac{\varepsilon\zeta\vec{E}}{6\pi\eta} \quad \ldots \quad \ldots \quad (20)$$

There remains to be discussed the approximation in the distribution of the countercharge inside the sphere.

For $\varkappa R = 0$ there is no countercharge inside the sphere, see fig. 1. When $\varkappa R = \infty$ there is actually a uniform distribution of the countercharge inside the sphere with density $\bar{\varrho}$. In both cases eq. (19) is correct.

For freely drained spheres (case c above), $u = ZeE/Nf$ irrespective of the distribution of the countercharge (compare also § 3). In case the sphere is impermeable (case d above) our approximation does not affect Z_{eff} and hence u is correct.

This shows that eq. (19) is correct in all limiting cases. For intermediate values of $\varkappa R$ and of $6\pi\eta R/Nf$ eq. (19) gives results which are slightly too high. This is because the approximation $\varrho = \bar{\varrho}$ in fact means that some of the countercharge is shifted from the centre of the sphere toward the surface, where its contribution to the electrophoretic effect is less than nearer the centre.

In order to check eq. (19) in the intermediate range we have compared it with the equation obtained by *Hermans* [4]), which involves an approximation in the hydrodynamic treatment, but uses the correct (*Hermans-Overbeek*) charge distribution. Eq. (19) gives slightly higher results than Hermans' expression for large $\varkappa R$ and large $6\pi\eta R/Nf$ and slightly lower results in the other extreme. The differences are all within 5 %, which suggests that both approximations are suitable.

Hermans and *Fujita* [3]) have dealt with the present problem without using any approximation. Their final expression, however, gives $u < ZeE/Nf$ for some intermediate value of the parameters. This is clearly impossible and further comparison must await a correction of the rigorous treatment.

§ 3.   Electrophoresis of polyelectrolytes.

Equation (19) for the electrophoresis of a porous sphere has been developed for polyelectrolytes with the provision that they are spherical coils to which the Hermans-Overbeek distribution of the counter ions applies. This distribution disregards the relaxation effect and the ionic atmospheres around the individual ions attached to the coil. This procedure is justified in solutions of low ionic strength, that is to say for low values of $\varkappa$. If $\varkappa$ is high, however, the interaction between single
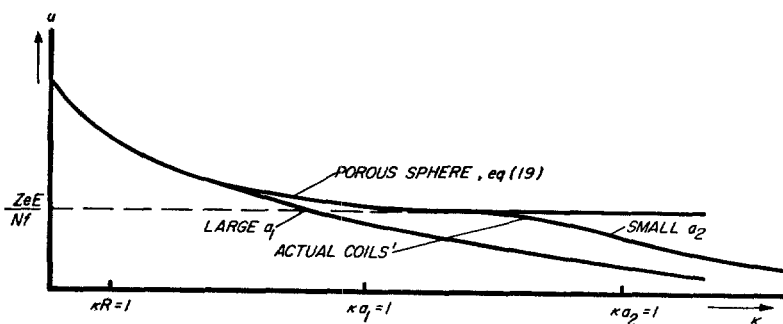

Fig. 4.   Schematic comparison of electrophoresis of porous
sphere and polyelectrolyte coils.

ions becomes an important factor, which is not taken into account by eq. (19). The range of validity of eq. (19) is shown schematically in fig. 4. The important dimensions are the radius R of the coil and the radius a of a charged monomer, for which two examples are given. In the range $\varkappa a \ll 1$ the local interactions discussed above may be neglected and the porous sphere model is suitable. However, when $1/\varkappa$ becomes comparable with a, the mobility of the coil will drop below the minimum value ZeE/Nf found for the porous sphere and eventually tends to zero with increasing $\varkappa$.

Although the porous sphere model has no quantitative value for large $\varkappa$, the conclusion that for large $\varkappa$ the system behaves as if it were fully drained remains valid for polyelectrolyte coils of arbitrary shape. This can be demonstrated with the aid of a different model.

In fig. 5 the coil is pictured as a thread. Each section of the thread is enveloped by a double layer of cylindrical symmetry.

Hydrodynamic interaction between different sections of the thread, i.e. partial draining, is observed when the liquid velocity produced by, say, section P reaches other sections, say, Q.

It follows from *Henry*'s treatment of the electrophoresis of the

cylindrical rod [8]) that the liquid velocity produced by section P vanishes outside the double layer enveloping P. Therefore, roughly speaking, the overlap of the double layers around P and Q is a measure for the mutual hydrodynamic interaction between these sections of the chain. Consequently the coil will be freely drained in electrophoresis when the
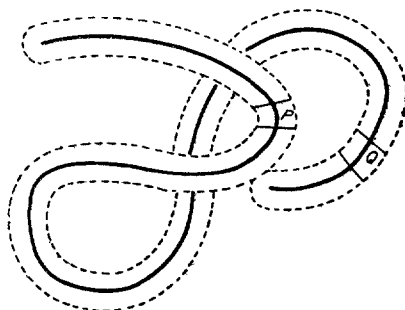

Fig. 5. Schematic picture of coiled polyelectrolyte
chain with electric double layer.

thickness of the double layer is small compared with the average distance of approach between various parts of the chain, that is to say if $\varkappa R \gg 1$.

It is anticipated that highly charged coils will always be nearly freely drained for any value of $\varkappa R$, because electric repulsion between different sections of the flexible chain will prevent significant overlap of the respective parts of the double layer. The electrophoretic mobility of a free drained coil is the same as that of the fully stretched and randomly oriented chain. Hence one may in this case apply *Henry*'s theory of the electrophoresis of an uniformly charged cylinder [8]). For random orientation the velocity of the rod is

$$\vec{u} = \frac{\varepsilon\zeta}{6\pi\eta}\,\vec{E}$$

Applying this equation to actual cases, the ζ potential should be interpreted as the average potential along the stretched chain. It is obvious that ζ and therefore $\vec{u}$ is very insensitive to the chainlength provided that $1/\varkappa$ is much smaller than this length.

Fitzgerald and *Fuoss* [9]) performed electrophoresis experiments on poly-4-vinyl-N-n-butyl-pyridinium bromides and found no significant difference between the mobilities of fractions of various molecular weights. With partial draining one expects a small dependence of the

[8]) *D. C. Henry,* Proc. Roy. Soc. London **A 133**, 106 (1931).
[9]) *E. B. Fitzgerald* and *R. M. Fuoss,* J. Polymer Sci. **14**, 329 (1954).

mobility on R (compare fig. 3) and hence on the molecular weight. Thus it seems that the compounds investigated by *Fitzgerald* and *Fuoss* were freely drained under the experimental conditions.

A final remark may be made on the ζ potential computed with *Henry's* equation from experimental data. *Alfrey, Berg* and *Morawetz* [10]) have solved the Poisson Boltzmann equation for a system of uniformly charged rods. Their application to polyacrylic acid shows that for degrees of ionisation from 0.5 to 0.9 some 50 % of the counter ions are accumulated very close to the surface of the rods for any value of $\varkappa$. This means that in solutions of highly charged polyelectrolytes a large fraction of the counter ions is more or less associated with the chain and move along with it in electrophoresis. Hence the charge computed from experimental values of ζ is in general much lower than the charge as determined, for instance, by titration.

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[10]) *T. Alfrey, P. W. Berg* and *H. Morawetz,* J. Polymer Sci. **7,** 543 (1951).